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20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

The self-diffusion coefficients of ^{14}C in NbC_x single crystals have been measured as a function of composition in the temperature range 1900-2315K, and can be represented by the expressions

$$D_C^*(NbC_{.84}) = (2.59^{+1.85}) \exp\left(-\frac{100.2 \pm 2.2 \text{ kcal/mol}}{RT}\right) \text{cm}^2/\text{s}$$

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$$D_C^*(NbC_{0.834})=(7.44^{+9.36}_{-4.14})\exp\left(\frac{105.0 \pm 3.3 \text{kcal/mole}}{RT}\right)cm^2/s$$

$$D_C^*(NbC_{0.766})=(2.22^{+1.98}_{-1.04})\times10^{-2}\exp\left(\frac{76.02 \pm 2.7 \text{kcal/mol}}{RT}\right)cm^2/s$$

The lower values of the activation energy and the pre-exponential term in
$NbC_{0.766}$ are attributed to a change in the path of C mass transport from that
of an octahedral-tetrahedral-octahedral mechanism in $NbC_{0.868}$ and $NbC_{0.834}$ to
one involving a C-metal divacancy mechanism. The effect of lattice geometry
and the electronic charge distribution on the diffusion mechanism is also
discussed.

The self-diffusion of ^{95}Nb in single cyrstals of $NbC_{0.868}$, $NbC_{0.834}$ and
$NbC_{0.766}$ has also been studied in the range of 2370-2660K. The diffusion
coefficients are composition independent and can be described by the expression:

$$D_{Nb}^*=(4.54^{+...}_{-1.75})\exp\left(-(140.0 \pm 2.4 Kcal/mole)/RT\right)cm^2/sec$$

An analysis of the results indicates that Nb diffuses by an (O-O) mechanism,
just as a pure metal diffuses in a f.c.c. lattice, wherein the atom migrates
from its lattice position directly to an analogous vacant site. As this
process involves the energies of both migration and Nb vacancy formation,
the slower diffusion rates of this species, relative to that of C whose
mechanisms of transport involve only the energy of migration, are thus
explained.

The conceptual design and construction of an apparatus developed for de-
forming materials by subjecting them to constant compressive stresses at
elevated temperatures is also described. The results of actual creep
studies have shown that all compositions undergo rapid and extensive primary
creep even at low stresses ($5-10 \times 10^3$psi) and temperatures (1400-1650°C) at
the onset of loading. Steady state conditions occur only after many hours
(days) have elapsed. The steady state exponent is between 4.2 and 4.5
which endicates a diffusion controlled mechanism of creep.

Table of Contents

DIFFUSION AND CREEP IN NIOBIUM CARBIDE AS A FUNCTION
OF TEMPERATURE AND CARBON CONTENT

I. Statement of Problem

The transition metal carbides possess a combination of some of the highest melting points, hardness values and mechanical strengths of any known materials. The contemporary interest in these materials in structural and cladding applications at temperatures where most materials would be molten or would seriously degrade made it imperative that the high temperature diffusion and deformation processes and their relationship to each other be understood. Thus, the principal thrusts of this ARO-sponsored program have been the conduct of self-diffusion studies of ^{14}C and ^{95}Nb in single crystals of $NbC_{0.868}$ $NbC_{0.834}$ and $NbC_{0.766}$ and constant stress compressive creep research on the same materials. Extensive characterization of these materials has also been performed.

II. Summary of Important Results

A. Diffusion Studies

1. Carbon

Typical penetration profiles for ^{14}C diffusion in the single crystal specimens of NbC_x (x=0.868, 0.834 and 0.766) showed high activity deviations from the straight line extrapolated from the deeper section of the profiles toward the "near-surface" (x·0) portion except those in which the tracer was implanted by diffusion into the crystals at low (=1673K) temperatures, the residual tracer removed mechanically and a NbC_x disk placed atop the crystal during the higher temperature diffusion anneals. The "near-surface" portion of the profiles was investigated in this program of research and found to be caused by factors extrinsic to the crystal itself, principally the delayed entry into the crystal of that portion of the tracer which is not initially in contact with the crystal. A complete discussion of this phenomenon from the standpoint of this research and that of others is presented in Ref. 1 of the bibliography. No evidence of high diffusivity path contributions to the volume diffusion was noted in the profile.

The linearity of the relative activity vs x^2 plots in the deeper sections of the profiles or the total profiles derived from the 1673 K implanted and covered samples indicates that these sections satisfy the solution to Fick's second law for concentration independent diffusion from a thin-film source. As such the calculated values of the diffusion coefficient, D_c^*, represent volume self-diffusion alone. The resulting curves produced from the plot of the logarithm of these D_c^* values vs $1/T$ for each composition, Figs. 1a-c, reveal an excellent fit to the classical Arrhenius equation and, with the use of computer-aided least-mean-square curve fitting, may be expressed as

$$D_c^*(NbC_{0.868})([110]) = (2.59_{-1.0}^{+1.82}) \times exp(-100.4 \pm 2.2 kcal/mol)/RT)cm^2/s \quad (1)$$

$$D_c^*(NbC_{0.834})([100]) = (7.44_{-4.14}^{+9.36}) \times exp(-105.0 \pm 3.3 kcal/mol)/RT)cm^2/s \quad (2)$$

$$D_c^*(NbC_{0.766})([110]) = (2.22_{-1.94}^{+1.98}) \times 10^{-} \times exp(-76.0 \pm 2.7 kcal/mol)/RTcm^2/s \quad (3)$$

The significant difference between the activation energies and pre-exponential terms of $NbC_{0.766}$ and the other two compositions indicates that at least two different C diffusion mechanisms are active in NbC_x single crystals in this range of C/Nb ratios and that the dominance of a particular mechanism is dependent on the composition. Furthermore, these results indicate that the dominant C diffusion mechanism in $NbC_{0.868}$ and $NbC_{0.834}$ is the same but different from that operative in $NbC_{0.766}$. The slightly higher activation energy in $NbC_{0.834}$ with increasing C deficiency relative to that of $NbC_{0.868}$ is consistent with the higher melting point of former material and is also found in TiC_x (2, 3, 4) and ZrC_x (5). However, $NbC_{0.766}$ has approximately the same melting temperature as $NbC_{0.868}$ and the largest C deficiency of these three compositions but a much lower activation energy for diffusion; thus, this is further evidence for the existence of two different C diffusion mechanisms. A discussion of the possible paths of transport are presented in the following paragraphs.

From a consideration of the rigid sphere NaCl-type structural model in which NbC_x forms and the activation energies determined in this research, there are three atomic paths for C diffusion which the present authors consider to be most probable. These are: (1) the (0-0) mechanism wherein the C atom

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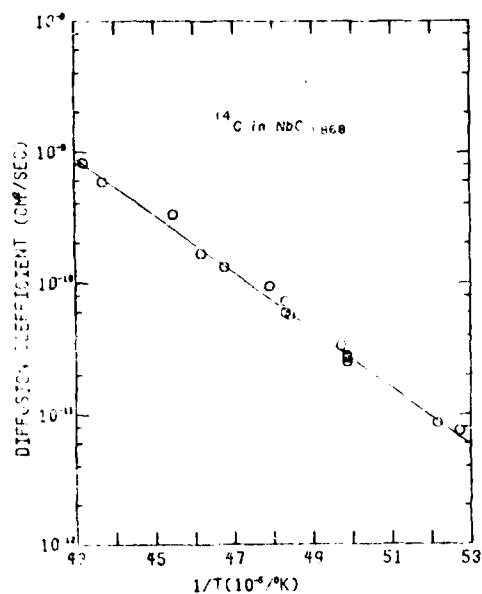
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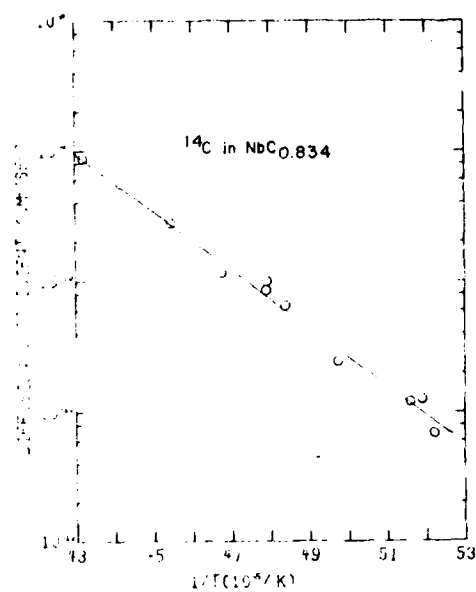
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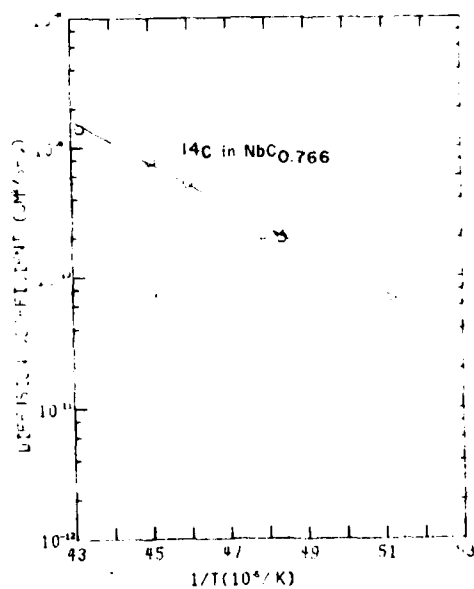
(c)

Fig. 1. Carbon-14 self-diffusion coefficients for the deeper sections of the
profiles plotted as a function of 1/T for (a) $NbC_{0.868}$, (b) $NbC_{0.834}$,
and (c) $NbC_{0.766}$.

jumps along the [110] direction directly to the nearest neighboring vacant C octahedral site with a jump distance $a_0/\sqrt{(2,2)}$ the (O-T-O) mechanism wherein the C atom jumps immediately to the nearest vacant C octahedral site via an unoccupied tetrahedral site formed by the Nb sublattice with an effective jump distance $a_0/\sqrt{2}$ and 3) the C-Nb transient "divacancy" mechanism wherein the C atom jumps to the analogous vacant C octahedral site by way of a normally occupied metal vacancy which has momentarily become associated with the C vacancy. This last mechanism has been discussed previously by Zagriazkin (6) and Andriyevskii and Gurov (7).

If only the strain energy produced in making the jump is considered, the ease with which the jump of each diffusion mechanism noted above can be made depends on the gap or separation between the metal atoms and the relative sizes of the C and metal atoms. Using 1.54Å as the atomic diameter of C and assuming the atomic diameters of the various metal atoms to be those of a hypothetical fcc metal lattice, the principal investigator has shown that the C and metal atoms are in contact along the [100] direction; however, gaps occur between the metal atoms in the [110] directions having a size, g_{110}, for NbC of 0.231Å. Since this size is much smaller than the size of the C atom, a large lattice strain or accommodating movement of the two Nb atoms is required in order for the former species to jump directly from one sublattice site to an adjacent vacant C site and therefore, by inference, for the (O-O) mechanism to be operative.

By comparison the shorter [111] jump which would be employed in the (O-T-O) mechanism would have the C atom passing directly through a much larger triangular gap in the (111) plane, g_{111}, and into a tetrahedral hole at the (¼, ¼, ¼) position in the carbide lattice. For NbC, $g_{111}=0.720$Å. In essence, two jumps are involved in going to-and-from the tetrahedral site; however, from a strain energy of migration viewpoint, of the two mechanisms, the latter would have the lower energy. The C vacancy formation component of Q would be the same in both cases.

However, from a consideration of the relative volumes of the C and Nb atoms, it is obvious that the energy of motion component in the activation energy in the C-metal transient "divacancy" diffusion mechanism will be much less than for the motion of the C atoms in the above two mechanisms;

since, in the latter processes, the C atom has to forcefully migrate
between Nb atoms. Therefore, it is concluded from a consideration of the
rigid sphere model and a comparison among these mechanisms that the energies
of C migration in the various mechanisms decrease in the order (O-O),
(O-T-O), C-Nb divacancy. As the Q of $NbC_{0.766}$ is less than that of the
other two compositions, the logical assignments from these points of view
are the divacancy path to $NbC_{0.766}$ and the (O-T-O) path to the other two
compositions. However, this does not explain why the transport mechanism
should change at the lower C concentration or why all compositions do not
follow the same lowest energy path. In order to understand this phenomenon,
one must also consider the changes in electronic charge densities in the
vicinity of the proposed avenues of transport.

In the hard sphere model employed above, all vacancies have the same
properties regardless of their concentration. However Williams [8] has
reported that the scattering of the electrons by vacancies in the non-
stoichiometric crystals of TiC_x (x=0.8-0.97) was not linearly proportional
to the vacancy concentration and thus implied that the C vacancies do not
have the same properties in the different compositions. The same is
believed to also be true for NbC_x. More recently, Chadi and Cohen [9],
in their theoretical research on the charge densities in NbC, have shown
that in going from NbC_1 to $NbC_{0.75}$ 1) the number of valence electrons is
reduced from 9 to 8 and 2) the magnitude of the charge in the peak of the
d_{xy} component of the d_ε states becomes nearly zero in the latter material.
Because of the extension of the d_{xy} electron orbits from the neighboring
Nb atoms into the metal vacancy, the C atoms diffusing through the metal
vacancy would have a barrier unless the electron density in the d_{xy} peak
were close to zero. Thus, the feasibility of the C-Nb transient divacancy
mechanism is enhanced as the C/Nb ratio decreases to a value close to 0.75.
Such evidence lends considerable support to the choice of the divacancy.
mechanism for C in $NbC_{0.766}$ as noted above, but the theoretical treatment
also provides information as to the choice of a path of transport for the
other two compositions.

The presence of the large number of structural C vacancies in all
compositions would indicate that the activation energy for the (O-T-O) and the
transient divacancy mechanisms would consist essentially of the C migration
energy in the former and the energy of Nb vacancy formation in the latter
path of transport.

From vapor pressure data, Storms et.al. [10] have calculated the Nb vacancy formation energy for $NbC_{0.750}$ to be 60.49 kcal/mol. Given the fact that there is no doubt some small energy of C migration associated with the divacancy mechanism, this value for the formation of the Nb vacancy is in line with 76.0 kcal/mol Q value found in $NbC_{0.766}$ and supports the conclusion that this mechanism is operative in this material.

2. Niobium

The ^{95}Nb diffusion coefficients calculated from the individual profiles using the thin film solution to Fick's second law obey closely the classical Arrhenius equation for all three compositions of NbC_x. With the use of computer assisted least-mean-square curve fitting, these coefficients may be expressed* as:

$$D_{Nb}^*(NbC_{0.868})([110]) = (8.99_{-4.82}^{+11.37})\exp(-(143.5\pm3.8 \text{Kcal/mole})/RT)\text{cm}^2/\text{sec} \quad (5)$$

$$D_{Nb}^*(NbC_{0.834})([100]) = (2.00_{-0.95}^{+1.79})\exp(-(135.7\pm3.2 \text{Kcal/mole})/RT)\text{cm}^2/\text{sec} \quad (6)$$

$$D_{Nb}^*(NbC_{0.766})([110]) + (6.61_{-4.74}^{+16.69})\exp(-(142.0\pm6.3 \text{Kcal/mole})/RT)\text{cm}^2/\text{sec} \quad (7)$$

The ^{95}Nb self-diffusion coefficients in these three compositions are nearly equal to one another and thus appear to be essentially independent of the C/Nb ratio. These results are similar to those reported by Sarian (11) for ^{44}Ti in TiC_x. This is also graphically illustrated in the combined plot of D_{Nb}^* as a function of 1/T shown in Fig. 2 for the three NbC_x compositions. This resulting curve can be expressed as:

$$D_{Nb}^*(NbC_x) = (4.54_{-1.75}^{+2.85})\exp(-(140.0\pm2.4 \text{Kcal/mole})/RT)\text{cm}^2/\text{sec} \quad (8)$$

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*The notation at the right of $D_{Nb}^*(NbC_x)$ indicates the crystallographic direction of ^{95}Nb transport; the limits on the preexponential term (D_0) and the activation energy (Q) are the probable errors.
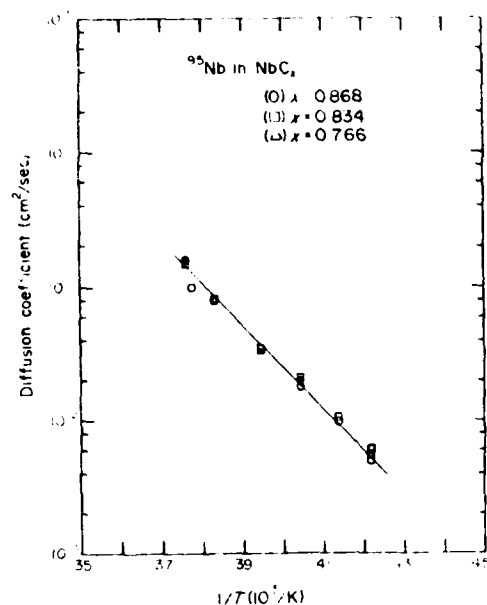
Fig. 2. Niobium-95 self-diffusion coefficients vs the reciprocal of the absolute temperature for NbC$_x$ (x = 0.868, 0.834 and 0.766)

The possible mechanisms of migration of the Nb atoms to the nearest Nb lattice vacancy in the NaCl structure of these three compositions are the same as that described above for C diffusion. In materials such as NbC$_x$ wherein the metal atom contains a partially filled d shell and the constitutents are octahedrally coordinated, a portion of the directions of the d_ϵ and d_γ electron states* in the octahedron around C may be schematically portrayed as shown in Fig. 3. Because of the extension of the Nb d_γ electron states into the C vacancy and the resultant repulsive forces which would be felt by a Nb atom in this position and, more importantly, the much smaller size of the C vacancy compared to that of the Nb atom, the migration energy for the latter atom through the C vacancy will be extremely high. Furthermore, the efficacy of this divacancy mechanism would be dependent on the concentration of C vacancies which is contrary to composition-independent coefficients experimentally determined for the ^{95}Nb diffusion. Thus, it is concluded that the Nb atom does not diffuse via the C vacancy.

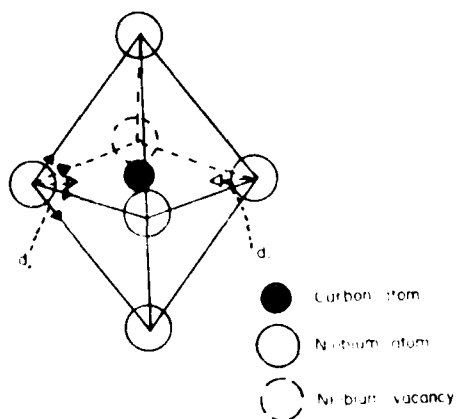*The d_ϵ states are d_{xy}, d_{yz} and d_{dx} and the d_γ states are $d_{x^2y^2}$ and $d_{3z^2-r^2}$.

Fig 3 Some of the directions of the d_γ and d_ϵ states in NbC, octahedron. The d_ϵ states of the Nb atoms are directed toward the C atoms and interact with the $2p$ states of C, the d_γ states are directed toward other Nb atoms and form Nb-Nb bonds.

From a general consideration of the (O-O) and the (O-T-O) mechanisms in NbC_x, the ^{95}Nb migration energy depends on the size of the gap relevant in each mechanism which the Nb atoms must pass through to reach the analogous vacancy. Using the values of 1.54 and 2.92 Å for the atomic diameters for C and Nb, respectively, the gap size, $g_{Nb[110]}$, encountered by the ^{95}Nb in diffusing along the (O-O) path is calculated to be 1.6 Å, which is larger than the 0.04 Å diameter of the tetrahedral site; thus, it is concluded that Nb atoms diffuse by the (O-O) mechanism in NbC_x.

The proper equation for the Nb self-diffusion coefficients in NbC_x, assuming a (O-O) diffusion mechanism, can be expressed as

$$D_{Nb} = f_{Nb} v_{Nb} a_0^2 \exp((S_{mNb} + S_{vNb})/R) \exp(-(H_{mNb} + H_{vNb})/RT) \qquad (9)$$

where f_{Nb} is the correlation factor, v_{Nb} the Nb jump frequency, a_0 the lattice parameter, S_{mNb} and H_{mNb} the entropy and enthalpy, respectively, for Nb atom migration and S_{vNb} and H_{vNb} the entropy and enthalpy, respectively, for Nb vacancy formation.

The composition dependence of the enthalpy of formation of the Nb vacancy in NbC_x has not been reported. However, Kaufman and Clougherty [12]

and Chang [13] have employed the Schottky-Wagner [14] model of defective phases to derive the expression

$$\Delta\bar{G}_M = -G^+_M +RT\ln[(1-x)/4]-2RT \ln \alpha \qquad (10)$$

where $\Delta\bar{G}_M$ is the partial free energy of formation for the metal species, G^+_C is the free energy to form the metal vacancy, x is the carbon/metal atom ratio and α is the ratio of the vacant lattice sites to the total lattice sites at stoichiometry ($x=1.0$). The vacancy concentration at stoichiometry was assumed to be less than 1. Kaufman and Sarney [15] further assumed that $RT \ln \alpha = \Delta H^o_f(0K,x=1.0)$ where ΔH^o_f is the standard enthalpy of formation of the Nb vacancy. Storms et al. [16] have reported this value as -33.47kcal/mole. Although this last parameter may vary slightly with an increase in temperature as well as a change in the C/metal ratio, it is obvious that a large portion of the total activation energy for Nb diffusion in NbC_x is used for migration.

The similarity in values of the ^{95}Nb diffusion coefficients of the three different single crystals strongly suggests that the transport of the Nb in the metal sublattice is uncorrelated with the changing number of C vacancies. Furthermore, the structural arrangement and the octahedral-octahedral diffusion mechanism herein postulated for the Nb atoms in NbC_x are equivalent to the atomic arrangement and transport process found in elemental f.c.c. metals. In this regard, Shewman [17] has presented an empirical expression for obtaining the activation energy Q, for self-diffusion in f.c.c. metals. This relationship is given by $Q/T_m \approx 36cal/K$ where T_m is the absolute melting point of the metal. Using $T_m = 3873K$ for niobium carbide, the Q is found to be 139.4kcal/mole which is in excellent agreement with the experimental value of ~140kcal/mol obtained in this research.

A comparison of the C and Nb-self-diffusion coefficients in all NbC_x compositions reveals that the former species diffuses more rapidly than the latter throughout the temperature range of this research. The reasons for these differences are primarily incorporated in the values of the terms which compose the activation energies for transport of the two atoms. In the case of C diffusion, in $NbC_{0.766}$ the migration energy necessary for this species to move through the large metal vacancy and into one of the numerous C vacancies is very small and the value of Q is principally that of the creation of the Nb vacancy.

Likewise, in $NbC_{0.868}$ and $NbC_{0.834}$, the presence of the large number of structural C vacancies suggests the value of Q is chiefly derived from the migration energy to and from the tetrahedral site in the (O–T–O) mechanism. However, in the Nb diffusion mechanism described above the activation energy term must consist not only of the energy of the migration of this species between the C atoms but also the energy of formation of the Nb vacancy.

B. High Temperature Creep Studies

1. Equipment Development

The need for reliable creep testing of ceramics has necessitated the design and fabrication of a new creep unit which can apply compressive stresses which are constant to within 1% for strains up to 10% can be applied to the sample and strains can be read with an accuracy of 5×10^{-7} m. Furthermore, loads as great as 440 kg can be applied to the samples and the furnace can be operated in vacuum or inert gas to 2573K or used with a muffle tube. Data acquisition, manipulation and plotting is computer controlled. This equipment has been described in detail in ref. (18), and will only be briefly outlined below.

The conceptual plans of the creep frame follow the fundamental concepts of Fullman, Carraker and Fisher[19] for the application of constant compressive stress loading using the Andrade fulcrum principle via a lever-arm mechanism from a weight pan loaded system. The equation

$$L_3 = \frac{L_1 L_2}{1}, \qquad (11)$$

where L_1, L_2 and L_3 are the distances between the various knife edges shown in Fig. 3, and l is the sample length, must be obeyed to maintain constant stress.
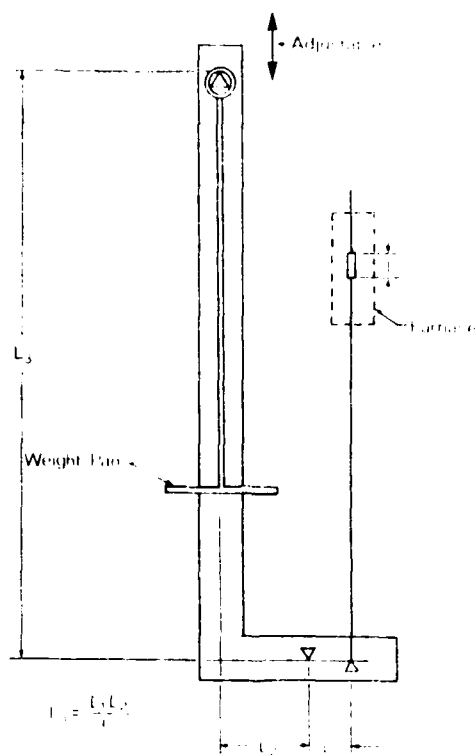

Fig. 3. Knife edge configuration for apparatus used in the present creep studies of SiC and NbC.

Two knife edges provide the fulcrum for the lever arm, another supports the weight pan, and a fourth applies the force to the lower sample push rod. When the load pan support columns are vertical, the frame acts as a simple fulcrum to apply a force on the lower push rod which is greater than the force on the weight pan by a factor of L_2/L_1. When the sample deforms, the frame tilts backward and the columns are no longer vertical. This movement increases the force applied to the push rod (and, therefore the sample) which is proportional to the preset L_3 and the amount of deformation. The increase in force compensates for the increase in area of the sample as it is compressed, thus maintaining a constant stress. Shorter samples require

a greater L_i because the area of the sample becomes greater for the same amount of deformation than it would for a sample of greater height. Sample area is not important in making L_i calculations because changes in area for a given amount of creep are of the same proportion for samples having either a large or a small area, if both are the same height.

The unit maintains constant stress to within 1% as long as the total strain does not exceed 10% and the experiment is initiated with the weight pan support columns in a vertical position. However, if some idea of the total strain during the run can be predicted and the unit is set such that it passes through the vertical position when approximately one-half of the strain has occurred, the stress can be held to within 0.5% up to a total strain of 10%. Two jacuators which raise and lower the main knife-bearing plates are used to make this adjustment and are linked to move simultaneously by turning a single handle.

Sample deformation is measured by an LVDT ultra-precise gauge head coupled to a signal conditioner which has a gauging range of $\pm 5.08 \times 10^{-4}$ m, a repeatability of 1.016×10^{-7} m, and a linearity of ± 0.2 of full scale. Since the nonlinearity is repeatable, it is possible to increase the accuracy of the creep measurements by performing a polynomial regression on the calibration curve instead of a linear regression. Three curves containing 51 points each over the range $(0 \text{ to } 5) \times 10^{-4}$ m were made for the LVDT employed in the creep experiments using a micrometer calibration stand. The data points were then run through a computer routine whose function is to find the polynomial that best fits the curve. However, the sum of the squared residuals must be at least 1% lower than the next lower order polynomial and must result in a noticeable improvement in reduction of the residual pattern. For the LVDT system employed in the present research, a cubic polynomial is most satisfactory and yields a standard deviation of 4.03×10^{-7} m. This last value is also the smallest amount of deflection which can be accurately measured with the equipment.

The previously mentioned signal conditioner which powers the LVDT outputs a dc voltage in the range ± 10 V which is proportional to the LVDT deflection. This output is fed into a digital dc voltmeter which reads

±10 V to a tenth of a millivolt. The voltmeter has a digital output and is interfaced to a mini-computer, which has been programed to take one voltage reading per minute. The computer program is also used to store the data on magnetic tape and to calculate true strain. The latter is output to one-channel of a two channel flatbed recorder via a digital to analog converter which is also interfaced to the computer. The other channel of the recorder is wired in parallel with the dc voltmeter to directly record the voltage output of the LVDT.

After a series of tests have been completed, the computer calculates the strain rate, the activation energy, the stress dependence, and performs any desired statistical analysis. A digital plotter produces graphical reproductions of the data in any of a host of possible formats.

2. Creep Research

The principal investigator has also initiated limited constant stress compressive creep. Studies have been conducted on the same single crystals of NbC_x as those used in the diffusion research. This research is still ongoing, and a renewal proposal for its continuation is now under review. The results and tentative conclusions of this research, as of this writing, are briefly reported below.

Samples 0.200 in. dia. by 0.300 in. high have been ultrasonically tre-panned from sections cut from the lengths of the three single crystal boules. The diffusion effort necessitated the use of only a small amount of material from each boule and, therefore, the composition did not measurably change from piece to piece within a given boule. The composition from one end of the boule to the other does vary slightly ($x = \pm 0.02$), however, as determined by lattice parameter measurements of each of the creep samples. The compositions noted below are therefore nominal compositions and are slightly. different from those noted in the diffusion discussion.

To date, considerably time has been consumed in learning to prepare pre-cisely cut and polished samples and in determining the CNb ratios. Neverthe-less, as of this writing, ten creep experiments lasting in excess of 1.5 weeks each have been conducted on samples previously annealed at 2000°C for 8 hours to remove residual stresses. Such long term experiments are required

because it takes a very long time (often in excess of two days) for a sample to reach a steady state condition of constant strain rate for a given stress and temperature. The use of on-line computer calculations of true strain and strain rate and the subsequent storage of this data allows one to determine when steady state conditions have been reached in a given segment of a run. More information concerning the creep equipment and experimental procedures is presented in the Plan of Research.

We have found that all compositions undergo rapid and extensive primary creep even at low stresses (5-10 x 10^3 psi) and temperatures (1400 - 1650°C) at the onset of initial loading. This is repeated to a much smaller degree for every subsequent increase in stress on temperature. As noted above, steady state conditions do not occur, however, until many hours (days) have elapsed from tne time of application of the new stress or temperature. This could easily explain why no previous investigator has established steady state conditions in any of the reported deformation or creep experiments.

Most of the creep research to date has been conducted at varying stress levels at a given temperature in order to determine the steady state stress exponent, n. This value has been determined to be between 4.2 and 4.5 for all three compositions, as shown in the representative graph, Fig. 4b, of $NbC_{0.81}$ for T = 1400°C. The corresponding overall creep curve for this sample is shown in compressed form in Fig. 4a. These values are indicative of a diffusion-controlled mechanism of creep; however, a final analysis awaits extensive TEM on the undeformed and the progressively deformed materials. Equipment for thinning the many samples both electrochemically or by ion milling is either now established or on order.

Only preliminary research has been conducted to date in the determination of the activation energy (Q) for steady state creep. However, .the extensive deformation of these very pure materials, even at low temperatures and the small effect of increased temperature on the strain rate have resulted in fairly low activation energy values. Although several additional experiments are necessary to confirm these tentative results, it is apparent that lattice self-diffusion does not play a role in the steady state creep process.
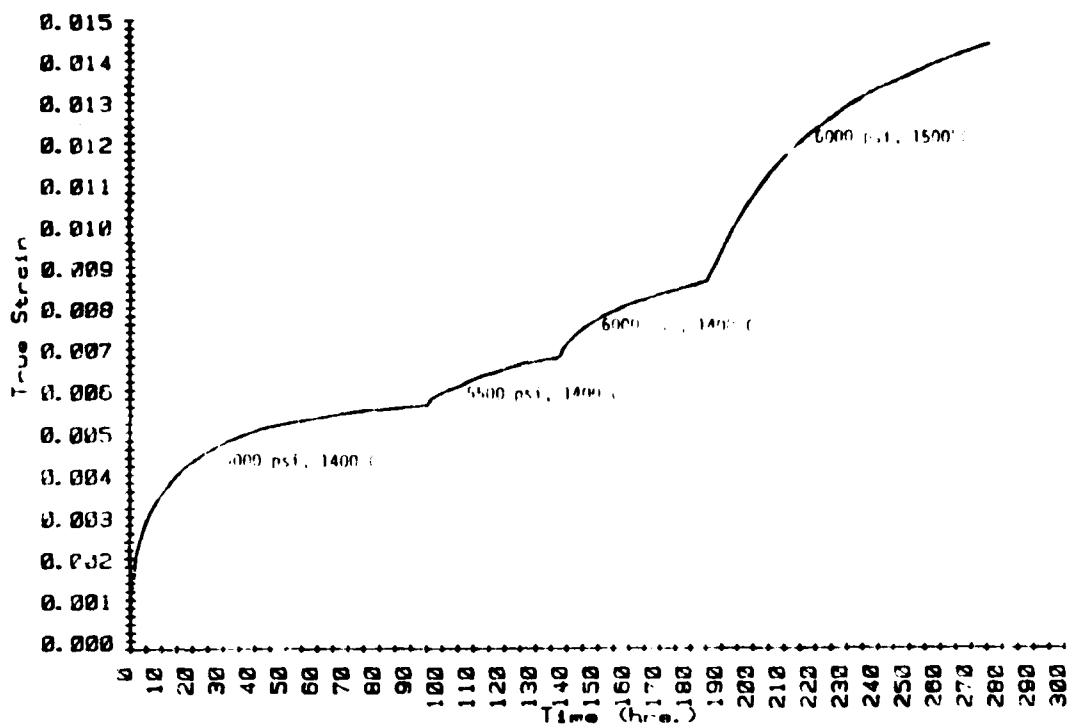
Fig. 4a. Creep curves sequentially obtained during a single run using three different constant stresses and two different temperatures.
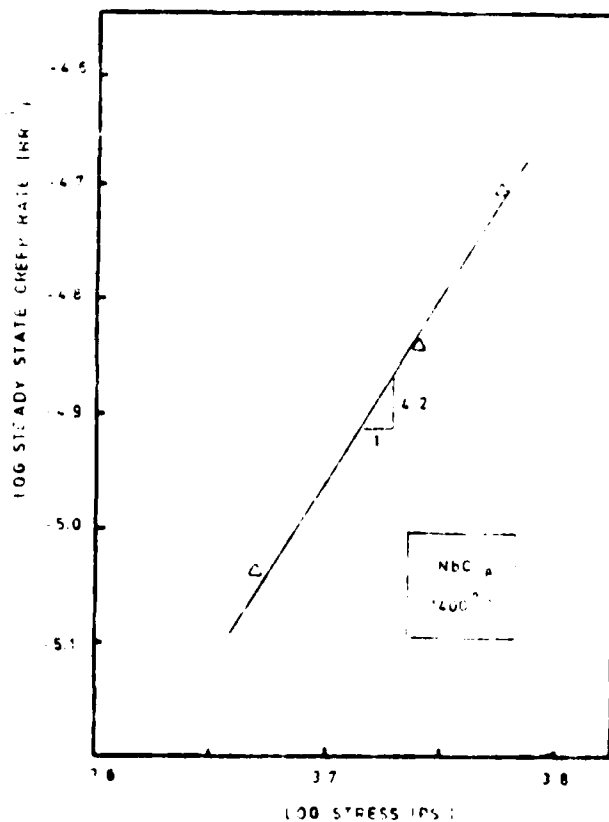

Fig. 4b. Steady state creep rate values as a function of stress using data derived from creep curves shown in Fig. 4a.

III. Publications Derived from this Grant

1. *J. D. Hong, W. E. Griffin and R. F. Davis, "Precision Grinding Device for Radioactive Tracer Diffusion Studies in Very Hard Ceramic Materials," Rev. Sci. Instrum. 49, 83-85 (1977).

2. *B. B. Yu and R. F. Davis, "Near Surface Effect (NSE) in Self-Diffusion in NbC_x," Physica Status Solidi (a) 51, 261 (1979).

3. *B. B. Yu and R. F. Davis, "Thermo-Mechanical Behavior of Unannealed NbC Single Crystals," J. Mat. Sc. and Eng. 39, 275 (1979).

4. *M. Hon and R. F. Davis, "Diffusion of ^{14}C in Polycrystalline β-SiC," J. Materials Science, 14, 2411 (1979).

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7. *B. F. Yu and R. F. Davis, "Diffusion of ^{95}Nb in Single Crystals of NbC_x," J. Chem. Phys. of Solids 41, 2088 (1980).

8. S. Chevacharoenkul and R. F. Davis, "Hot Isostatic Pressing of Niobium Carbide," to be submitted J. Mat. Sc. and Eng.

*Referred Publications

IV. Participating Scientific Personnel

1. Robert F. Davis, Principal Investigator, Professor of Materials Engineering, North Carolina State University, Raleigh, N. C.

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4. S. Chevacharoenkul, graduate research assistant, received M.S. degree May, 1979; is currently working toward Ph.D. degree under the supervision of Robert F. Davis.

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